



# The isothermal variation of the entropy ( $\Delta S_T$ ) may be miscalculated from magnetization isotherms in some cases: MnAs and $\text{Gd}_5\text{Ge}_2\text{Si}_2$ compounds as examples

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## ABSTRACT

The determination of the isothermal variation of the entropy ( $\Delta S_T$ ) is discussed in the present work. We show that  $\Delta S_T$  has very different profiles and magnitudes when calculated from  $M$  vs.  $H$  or  $M$  vs.  $T$  experimental data. For MnAs compound,  $\Delta S_T$  obtained from  $M$  vs.  $T$  data does not present a colossal peak. This result and the agreement between theoretical and experimental non-colossal magnetocaloric effect indicate that the colossal peak may be miscalculated from  $M$  vs.  $H$  experimental data. For  $\text{Gd}_5\text{Ge}_2\text{Si}_2$  compound,  $\Delta S_T$  obtained from  $M$  vs.  $T$  data does not present the peak observed in  $\Delta S_T$  from  $M$  vs.  $H$  data.

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## 1. Introduction

The entropic colossal magnetocaloric effect (CMCE) was first reported few years ago for MnAs compound submitted to hydrostatic pressures by Gama and co-workers [1]. In 2006, de Campos and co-workers [2] also reported CMCE results for the series  $\text{Mn}_{1-x}\text{Fe}_x\text{As}$ . The entropic CMCE is characterized by the overcoming of the magnetic limit of the entropy [ $S_M = R \ln(2J + 1)$ ], which is around  $100 \text{ J kg}^{-1} \text{ K}^{-1}$  for the compounds of the series  $\text{Mn}_{1-x}\text{Fe}_x\text{As}$ .

In a recent paper, Liu et al. [3] discussed the determination of the isothermal variation of the entropy ( $\Delta S_T$ ) in materials that present first-order magnetic transition. They suggested that the colossal  $\Delta S_T$  peaks presented by MnAs compound under pressure [1] and compounds of the series  $\text{Mn}_{1-x}\text{Fe}_x\text{As}$  [2] are spurious. The authors also claimed that pronounced peaks in other series of compounds previously reported, such as  $\text{Gd}_5(\text{Si}_{1-x}\text{Ge}_x)_4$  [4] and  $\text{Mn}_{1-x}\text{Sb}_x\text{As}$  [5], in spite of not colossal, may be unreal. Besides that, Liu et al. [3]

mentioned that the Maxwell relation

$$\Delta S_T(T)_{\Delta H} = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH \quad (1)$$

cannot be used in the vicinity of the Curie temperature because of the coexistence of paramagnetic and ferromagnetic phases and suggested an alternative “geometric” solution to remove the supposed spurious  $\Delta S_T$  peaks. After Liu et al. [3], other works also discussed the possible overestimation of the entropic magnetocaloric effect [6–13].

The discussion about the validity of the Maxwell relation (1) around Curie temperature is not new. In 1999, Giguère and co-workers [14] claimed that  $\Delta S_T$  could not be calculated using this Maxwell relation for materials presenting first-order transitions. After that, Gschneidner, Jr. and co-workers [15] affirmed that relation (1) could be applied to all available experimental data until that moment. More recently, de Oliveira and von Ranke [16] discussed the formulation of the Maxwell relation showing its limitation for the calculation of the magnetic entropy changes, around the first-order magnetic phase transition.

In the present work, we intend to show that we have to be careful with the application of the relation (1) on any available

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magnetization data, mainly with isothermal magnetization curves. From isofield magnetization ( $M$  vs.  $T$ ) data for MnAs compound and using the relation (1) we obtain the  $\Delta S_T$  vs.  $T$  curve, which does not present the colossal peak. This peak may occur when  $\Delta S_T$  vs.  $T$  curve is calculated from  $M$  vs.  $H$  data.  $\text{Gd}_5\text{Ge}_2\text{Si}_2$  compound does not also present any pronounced peak in  $\Delta S_T$  obtained from  $M$  vs.  $T$  data.

## 2. Materials and methods

The polycrystalline sample of MnAs analyzed in the present work is the same that was used in the Ref. [7]. The polycrystalline sample of  $\text{Gd}_5\text{Ge}_2\text{Si}_2$  is the same that was used in the Ref. [17]. Magnetic measurements have been performed in a SQUID magnetometer (Quantum Design).

The isofield magnetization ( $M$  vs.  $T$ ) curves for MnAs compound were measured increasing the temperature at the rate of 0.5 K/min and fixed magnetic fields with steps of 2 kOe up to 50 kOe. We easily see that increasing the magnetic field the magneto-structural transition displaces to higher temperatures. It occurs at a rate of around 0.35 K/kOe. After interpolating each isofield curve and taking derivatives in steps of 0.5 K, we used a numerical approximation of the relation (1),

$$\Delta S_T(T_j)_{\Delta H} = \sum_{i=1}^{n-1} \frac{1}{2} \left( \left( \frac{\partial M_i}{\partial T_j} \right)_{H_i} + \left( \frac{\partial M_{i+1}}{\partial T_j} \right)_{H_{i+1}} \right) \cdot \Delta H, \quad (2)$$

to calculate the isothermal variation of the entropy as a function of the temperature. In the relation (2),  $M_i$  and  $M_{i+1}$  are the experimental values of the magnetization at applied magnetic fields  $H_i$  and  $H_{i+1}$ , respectively, and temperature  $T_j$ ;  $\Delta H = 2$  kOe is the magnetic field step.

From the available isofield magnetization data, we are able to build isothermal magnetization curves, which are presented in Fig. 1b. It was used data with steps of 1 K, so neighbor isotherms in Fig. 1b are separated by 1 K. Using another numerical approximation of the relation (1),

$$\Delta S_T(T)_{\Delta H} = \frac{1}{2\delta T} \left( \delta M_1 \delta H_1 + 2 \sum_{k=2}^{n-1} \delta M_k \delta H_k + \delta M_n \delta H_n \right), \quad (3)$$

already discussed elsewhere [18], we calculated the isothermal variation of the entropy ( $\Delta S_T$ ).

The  $M$  vs.  $T$  and  $M$  vs.  $H$  curves for  $\text{Gd}_5\text{Ge}_2\text{Si}_2$  compound were also measured increasing the temperature and the magnetic field.

## 3. Results and discussion

When we calculate  $\Delta S_T$  from the measured isofield data for MnAs (Fig. 1a), we obtain a curve with no spike (open circles in Fig. 2a). When we calculate  $\Delta S_T$  from the mapped isothermal curves in Fig. 1b, we obtain a coincident curve, within the expected errors from the numerical procedures. Besides there is no spike in  $\Delta S_T$  data, the observed profile and values are similar to those reported previously [5].

For MnAs compound, when we measure the isothermal magnetization as a function of the magnetic field (solid symbols in Fig. 3) and compare with the  $M \times H$  curves obtained from  $M$  vs.  $T$  data (open symbols), we clearly notice great differences. The greatest one is the large areas between specific pairs of isotherms around  $T_C$  ( $\sim 319$  K), which are observed in the measured  $M$  vs.  $H$  data and are not observed in the mapped  $M$  vs.  $H$  curves from  $M$  vs.  $T$  data. These areas leads to the colossal spike in the magnetocaloric effect (MCE) shown in Fig. 2a (solid symbols). A more subtle difference between these two sets of isotherms is related to the position and displacement of the metamagnetic transitions. Equivalent isotherms of each set of  $M$  vs.  $H$  curves have different transition magnetic fields. It accounts for the different temperatures of the  $\Delta S_T$  maxima and the temperature ranges of the plateaus, as can be seen in Fig. 2a. The  $\Delta S_T$  plateau from  $M$  vs.  $T$  data is clearly larger than that from the measured  $M$  vs.  $H$  data and is shifted to higher temperatures. These features are due to large magnetic hysteresis at  $T_{PM}$  (transition temperature on heating and at zero magnetic field) and high thermal hysteresis at the highest magnetic field (50 kOe in this case), respectively. As shown in a previous work [7], the large magnetic hysteresis around  $T_{PM}$  is responsible for the huge  $\Delta S_T$  peak, not

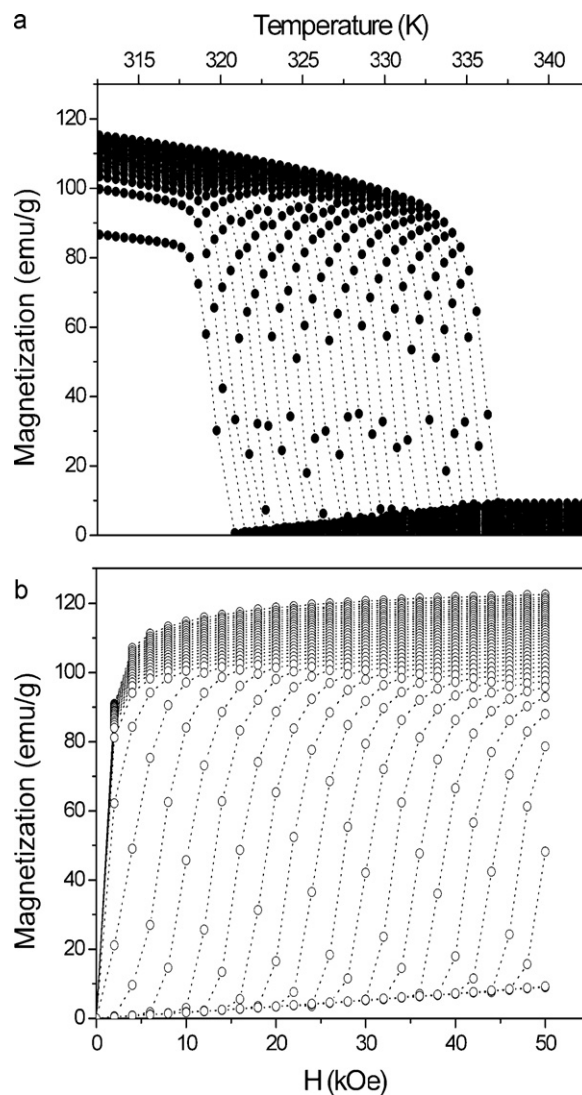
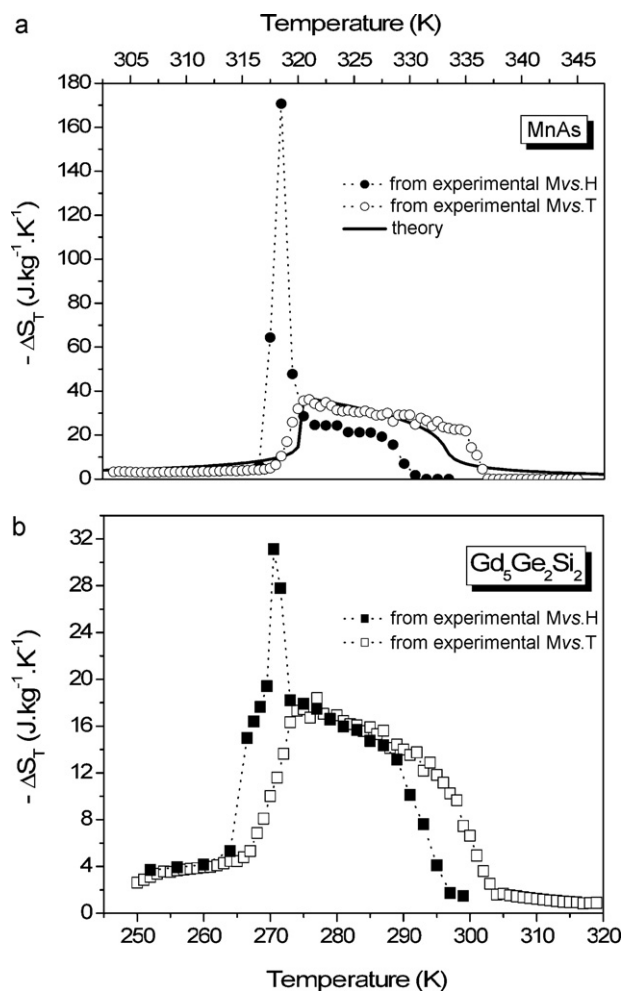


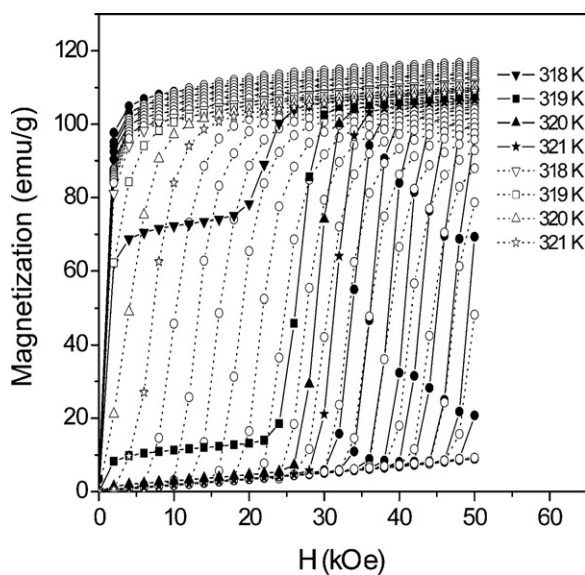
Fig. 1. (a) Magnetization isofields measured in magnetic fields from 2 kOe up to 50 kOe ( $\Delta H = 2$  kOe) for MnAs compound. (b) Magnetization isotherms obtained from the isofields. Dotted lines are guides for the eyes.

the thermal hysteresis as supposed by Caron et al. [9]. Since there is area (magnetic moment) conservation when we use Maxwell relation (1), the larger is the MCE spike the smaller is the plateau area.

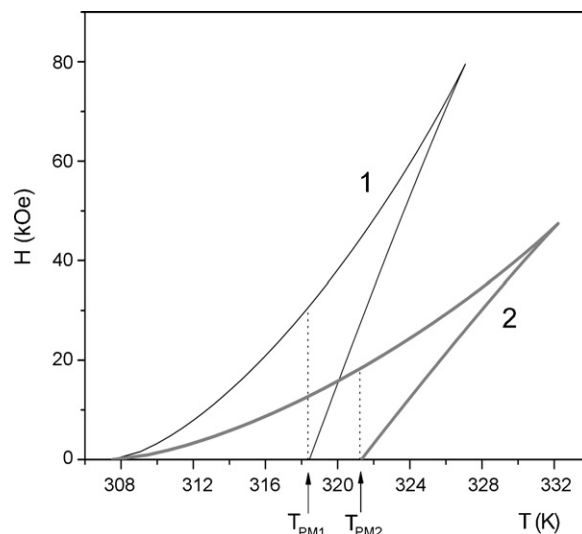
The difference between the magnetic and thermal hysteresis influence on the magnetization isotherms and  $\Delta S_T$  peak can be understood using the theoretical results in Figs. 4 and 5. In Fig. 4, we show theoretical  $H$ - $T$  diagrams obtained from the model presented in Ref. [7]. In each diagram, the temperature  $T_{PM}$  defines the transition from ferromagnetic to paramagnetic phase on heating. Besides, the  $\Delta S_T$  spike appears around this temperature. The dotted lines show the magnetic hysteresis around  $T_{PM}$  and it is easy to notice that magnetic hysteresis in diagram 1 is larger than that in diagram 2. At low magnetic fields, where  $T_C$  is around  $T_{PM}$ , the thermal hysteresis in diagram 1 is smaller than that in diagram 2. In Fig. 5, we show two sets of magnetization isotherms obtained from diagram 1 (Fig. 5a) and diagram 2 (Fig. 5b). It is clear that the area between isotherms around  $T_{PM}$  is larger in the set 1 (Fig. 5a). And this area defines the intensity of the  $\Delta S_T$  spike. Then, it is easy to observe that the larger is the magnetic hysteresis the larger is the  $\Delta S_T$  spike. Therefore, the magnitude of the  $\Delta S_T$  spike is directly affected by magnetic hysteresis.



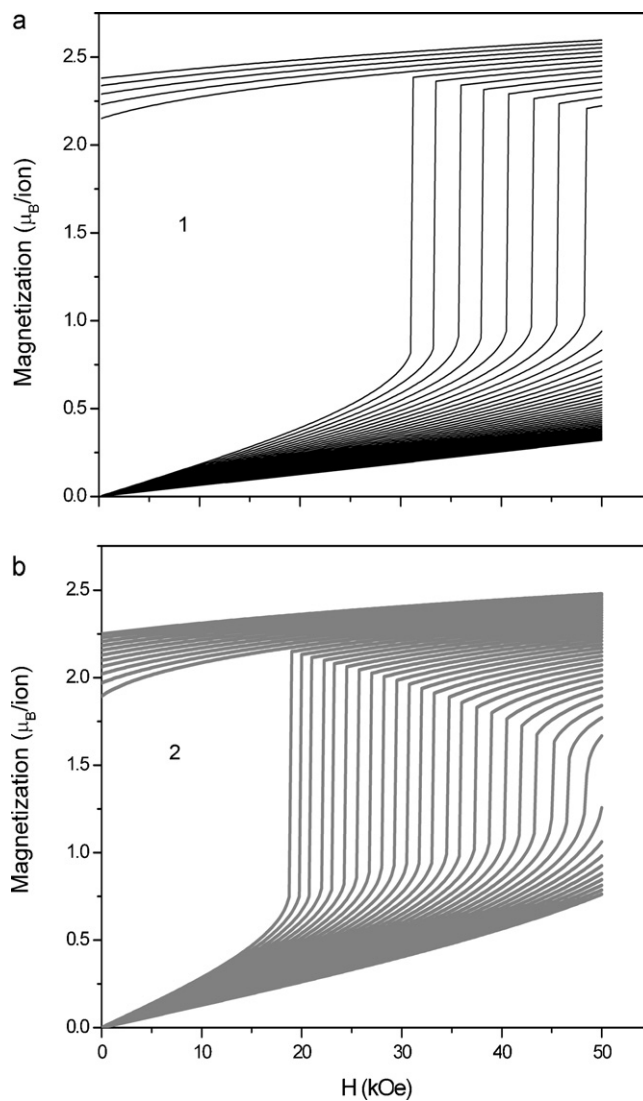
**Fig. 2.** (a) MnAs: isothermal variation of the entropy ( $\Delta S_T$ ) calculated as usual from the measured isotherms of Fig. 3 (solid symbols);  $\Delta S_T$  calculated as usual from isotherms of Fig. 1b (open symbols) and the theoretical  $\Delta S_T$  (line). (b)  $\text{Gd}_5\text{Ge}_2\text{Si}_2$ :  $\Delta S_T$  calculated as usual from  $M$  vs.  $H$  data (solid symbols);  $\Delta S_T$  calculated from  $M$  vs.  $T$  data (open symbols). Dotted lines are guides to the eyes.



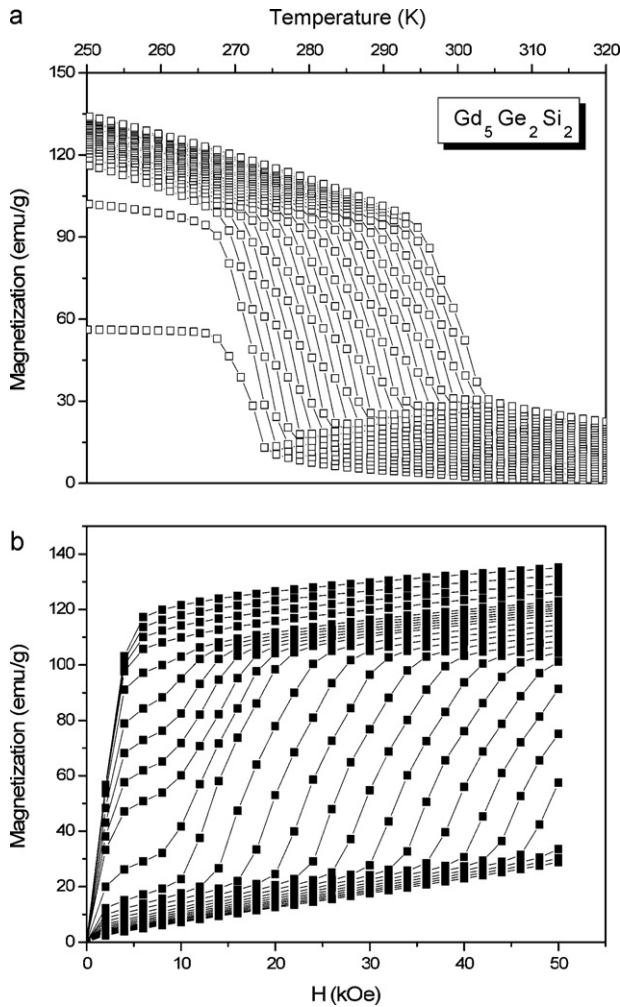
**Fig. 3.** Magnetization isotherms for MnAs compound measured from 310 K up to 334 K, with  $\Delta T = 1$  K from 316 K on (solid symbols), and magnetization isotherms of Fig. 1b (open symbols). Dotted and solid lines are guides to the eyes.



**Fig. 4.** Theoretical  $H$ - $T$  diagrams obtained from the model in Ref. [7].  $T_{PM1}$  and  $T_{PM2}$  are the transition temperatures from ferromagnetic to paramagnetic phases, on heating, for diagram 1 and diagram 2, respectively.



**Fig. 5.** Theoretical magnetization isotherms calculated with the same parameters used to obtain the diagram 1 (a) and diagram 2 (b). The temperatures of the isotherms are the same in the sets (a) and (b).



**Fig. 6.** (a) Magnetization isofields for Gd<sub>5</sub>Ge<sub>2</sub>Si<sub>2</sub> compound measured in magnetic fields from 2 kOe up to 50 kOe ( $\Delta H = 2$  kOe); (b) magnetization isotherms for Gd<sub>5</sub>Ge<sub>2</sub>Si<sub>2</sub> compound measured from 250 K up to 300 K, with  $\Delta T = 1$  K from 266 K up to 272 K. Solid lines are guide to the eyes.

The influence of the thermal hysteresis is not relevant in this case.

In Fig. 6, we show the experimental magnetization isofields (Fig. 6a) and the experimental magnetization isotherms (Fig. 6b) for Gd<sub>5</sub>Ge<sub>2</sub>Si<sub>2</sub> compound. It is clear the difference between these isotherms and those experimental isotherms for MnAs (Fig. 3). The absence of large areas in the isotherms for Gd<sub>5</sub>Ge<sub>2</sub>Si<sub>2</sub> is due to a relatively low magnetic hysteresis comparing with MnAs compound [19,20]. Nevertheless, the  $\Delta S_T$  profiles for Gd<sub>5</sub>Ge<sub>2</sub>Si<sub>2</sub> compound (Fig. 2b) have the same kind of shift in temperature presented by MnAs compound. Besides, the MCE spike obtained from  $M$  vs.  $H$  data does not exist in  $\Delta S_T$  obtained from  $M$  vs.  $T$ . Results from Caron et al. [9] for Mn<sub>0.99</sub>Cu<sub>0.01</sub>As and Gd<sub>5</sub>Ge<sub>2.3</sub>Si<sub>1.7</sub> compounds present peaks in  $\Delta S_T$ , which we suppose are also miscalculated, since they have used  $M \times H$  data to calculate  $\Delta S_T$ . The same assumption can be extended to important works, such as Refs. [1,2,4].

The thermodynamic Maxwell relation (1) presents a magnetization derivative with respect to temperature and should be applied to  $M$  vs.  $T$  data. Instead of using the numerical approximation for  $M$  vs.  $T$  data, relation (2), most of the works in the last years apply the numerical approximation for  $M$  vs.  $H$  data, relation (3). Probably for all reversible magnetic transitions, we could transform  $M$  vs.  $T$  data into  $M$  vs.  $H$  curves, which would be equal to the measured  $M$  vs.  $H$  data, and vice versa. Thus,  $\Delta S_T$  obtained from  $M$  vs.  $T$  or  $M$  vs.  $H$  data

(using relation (2) or (3)) should be equivalent. It is not true in the case of MnAs and Gd<sub>5</sub>Ge<sub>2</sub>Si<sub>2</sub> compounds, and certainly for several other first-order magnetic materials. In other words, the numerical approximation for  $M$  vs.  $H$  data, relation (3), may be applied to every reversible magnetic transition. However, it must be used with care for irreversible magnetic transitions, because it may be a poor approximation or even not valid for measured  $M$  vs.  $H$  data of several magnetic materials. For irreversible (hysteretic) processes, these relations are approximations and the validity of these approximations depends on the free energy difference among metastable and stable states. For MnAs compound, for instance, the calculated free energy presents low relative differences among metastable and stable states [7,17]. In a few cases,  $\Delta S_T$  obtained from  $M$  vs.  $H$  data may be a reasonable approximation, such as the results in Fig. 4b in Ref. [9] and Fig. 2b in Ref. [6]. If we measure isofields ( $M$  vs.  $T$ ) and calculate  $\Delta S_T$ , we will possibly obtain similar results.

Despite the divergences observed in the MCE obtained from two different measurement protocols, we verified that, within the estimated errors, the refrigeration capacity is the same in both cases for MnAs ( $\sim 520 \text{ J kg}^{-1}$  for  $\Delta T = 26 \text{ K}$ ) and Gd<sub>5</sub>Ge<sub>2</sub>Si<sub>2</sub> ( $\sim 540 \text{ J kg}^{-1}$  for  $\Delta T = 47 \text{ K}$ ). The refrigeration capacity ( $q$ ) is another important parameter that characterizes the MCE and it is given by [21–23]:

$$q(\Delta T)_{\Delta H} = - \int_{T_1}^{T_2} \Delta S_T(T)_{\Delta H} dT, \quad (4)$$

where  $\Delta H$  is the variation of the magnetic field used to calculate  $\Delta S_T$ ,  $T_1$  is the temperature of the cold end of a refrigeration cycle,  $T_2$  is the temperature of the hot end and  $\Delta T = T_2 - T_1$ . The refrigeration capacity is also directly related to the saturation magnetization of the material [24],

$$- \int_0^\infty \Delta S_T(T)_{\Delta H} dT = gJ\mu_B \Delta H, \quad (5)$$

where the saturation magnetization  $M_S = gJ\mu_B$ , and therefore it is expected the same value for every measurement protocols. The method proposed by Liu et al. [3] for eliminating the  $\Delta S_T$  spikes clearly modifies the values obtained for the refrigeration capacity when compared to the usual method. In the case of MnAs compound under hydrostatic pressure, there is an enormous reduction of the refrigeration capacity [3] and the magnetic moment as well, which seems not to be correct. In other methodologies presented in the literature [11–13], the magnetic moments calculated using Eq. (5) may also be underestimated.

It is also interesting to apply here the theoretical model used recently to explain the colossal magnetocaloric effect (CMCE) in MnAs [25] and compounds of the series Mn<sub>1-x</sub>Fe<sub>x</sub>As [2]. This model considers the Gibbs free energy in stable equilibrium. The Grüneisen parameter  $\gamma$  was introduced and certain non zero values of this parameter give rise to the CMCE. In the present work, we used a reasonable set of parameters, setting  $\gamma = 0$ , and the theoretical  $\Delta S_T$  as a function of the temperature is shown in Fig. 2a, which does not present the colossal peak. It is worth noticing that using  $\gamma = 0$  in the model from Ref. [16], the theoretical contribution to  $\Delta S_T$  from the lattice is canceled. The entropy calculated from a sixth-order Landau expansion also yields a giant MCE (GMCE) instead of CMCE [7]. Besides, when we compare the  $\Delta S_T$  for MnAs and Gd<sub>5</sub>Ge<sub>2</sub>Si<sub>2</sub> compounds obtained from the magnetization isofields with the  $\Delta S_T$  obtained from calorimetric data [10,19,20], we notice that all of them do not present the spike observed in the  $\Delta S_T$  obtained from magnetization isotherms (Figs. 3 and 6b, respectively).

Finally, it is worth stressing that there are  $\Delta S_T$  results obtained from calorimetric data for MnAs [10] and Gd<sub>5</sub>Ge<sub>2</sub>Si<sub>2</sub> [26,27] compounds, which are similar to our results obtained from  $M$  vs.  $T$  data. In all cases, instead of a spike around  $T_C$ , there is a maximum



followed by smooth decreasing values of  $\Delta S_T$ . From DSC measurements [28], the  $\Delta S_T$  around  $T_C$  for  $\text{Gd}_5\text{Ge}_2\text{Si}_2$  is about  $13 \text{ J kg}^{-1} \text{ K}^{-1}$ . For two other different samples of  $\text{Gd}_5\text{Ge}_2\text{Si}_2$  compound, the maximum  $\Delta S_T$  obtained from calorimetric data is about  $14 \text{ J kg}^{-1} \text{ K}^{-1}$  [26] and  $19 \text{ J kg}^{-1} \text{ K}^{-1}$  [27]. For our sample, the maximum  $\Delta S_T$  is about  $17 \text{ J kg}^{-1} \text{ K}^{-1}$ . For MnAs compound, the maximum  $\Delta S_T$  around  $T_C$  from calorimetric data is about  $29 \text{ J kg}^{-1} \text{ K}^{-1}$  for a field variation of 60 kOe [10], while our result for  $\Delta H = 50 \text{ kOe}$  is about  $36 \text{ J kg}^{-1} \text{ K}^{-1}$ . The main reason for the divergences among these values is probably the differences in sample preparation.

#### 4. Conclusions

We claim that  $\Delta S_T$  for first-order magnetic materials, mainly with relevant magnetic hysteresis, is not well determined from the magnetization data, since in irreversible processes the magnetization is not a state function, i.e., the magnetization depends on the processes of the variation of the thermodynamic coordinates  $H$ ,  $T$  and, possibly,  $P$  (pressure). In addition, we claim that the free energies should be analyzed in order to verify the approach to employ the Maxwell relations even on  $M$  vs.  $T$  data, which could be used to calculate  $\Delta S_T$  as a reasonable approach in some cases. Besides that, with an efficient methodology for calculating  $\Delta S_T$ , we should be able to obtain reasonable values of the magnetic moments of any magnetocaloric material, using relation (5). Finally, some experimental and theoretical results indicate that the colossal peak of  $\Delta S_T$  in MnAs and the  $\Delta S_T$  spike in  $\text{Gd}_5\text{Ge}_2\text{Si}_2$  (and probably in other compounds) may be miscalculated, but it does not mean that CMCE does not exist. To verify that, we suggest direct measurements of the heat flow ( $\delta Q$ ) to obtain the variation of the entropy. In fact, *direct*  $\delta Q$  measurements are appropriated to design optimal thermodynamic cycles and to calculate the refrigeration efficiencies, instead of the *indirect*  $\Delta S_T$  calculations, which need mathematical formulation prescriptions, usually accurate for reversible (hysteresis free) thermodynamic processes.

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